

VOLTAMMETRIC REDUCTION BEHAVIOUR AND ANALYSIS OF DICHLONE

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ABSTRACT: The voltammetric reduction behaviour of Dichlone has been carried out by d.c.polarography, cyclic voltammetry (CV), a.c.polarography and differential pulse polarography (DPP) in methanolic Britton-Robinson buffer of pH ranging 2.0-12.0. The nature of electrode process was studied, the number of electrons was evaluated and the reduction mechanism was proposed. Quantitative determination was carried out in the concentration range 1.0×10^{-5} M to 2.5×10^{-8} M using a DPP method with a lower detection limit of 2.0×10^{-8} M. The proposed method was successfully applied in the determination of Dichlone in grains, soils and water samples.

Key words: Dichlone; Reduction behaviour; Mechanism; Analysis; Environmental samples

INTRODUCTION

Dichlone [2,3-dichloro-1,4-naphthoquinone] (Figure 1) is a quinone group containing pesticide and is a class of aromatic diketones, in which the carbonyl groups form part of the ring system. Several quinone pesticides are commonly used to treat foliage diseases of some crops.

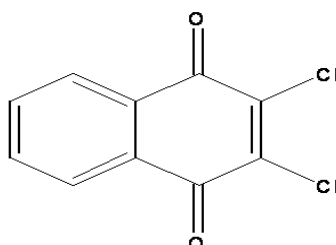


Figure 1: Structure of Dichlone

The electrochemical behaviour of quinones in aprotic media has been studied extensively. But most of the studies are devoted to understand the fundamental electrode processes [1]. Polarography has been used as an analytical method for quinone- hydroquinone system [2]. The applications are summarized and compiled periodically in Analytical Chemistry Annual Reviews [3]. Adkins and Cox [4] reported reduction potential of anthraquinone and phenanthraquinone in unbuffered tetramethyl ammonium hydroxide solutions [5]. Wawzonek et al [6] reported half-wave potentials for anthraquinones in buffered media. Edward et al [7] studied the polarographic behaviour of a large number of hydroxyl substituted benzoquinones, naphthaquinones and anthraquinones.

The purpose of this work is deals with the electrochemical reduction behaviour and analysis of Dichlone by using advanced electrochemical techniques such as d.c.polarography, cyclic voltammetry, a.c.polarography and differential pulse polarography and its determination in grains, soils and water samples by differential pulse polarography.

MATERIALS AND METHODS

Model 364 polarographic analyser supplied from PRC coupled with BD 8 Kipp and Zonen X-t recorder was used for d.c.polarographic measurements. Other techniques were carried out using a Metrohm unit: E 506 polarecord coupled with E 612 VA-scanner, E 648 VA-combistand, E 608 VA-controller, and a digital electronics 2000 X-Y/t recorder. All electrochemical three-electrode design at $25 \pm 0.1^\circ\text{C}$. The dropping mercury electrode (area: 0.0223 cm^2 , flow rate of Hg: 2.73 mg/sec , and mercury column height: 35 cm) and hanging mercury drop electrode (with an area of 0.0328 cm^2) were used as working electrodes. Reference electrodes employed were Ag/AgCl (s), Cl^- electrode for cyclic voltammetry, a.c.polarography, and differential pulse polarography and saturated calomel electrode (SCE) for d.c.polarography. Platinum electrode was used as counter electrode for all the techniques to complete electrolytic current. A modified cell with mercury pool cathode, SCE, platinum wire gauze electrode, and spot galvanometer, was used for controlled potential electrolysis. Dichlone was obtained from Cyanamid (India) Ltd., Bombay. The purity of the sample was tested by melting point determination and TLC analysis. Britton-Robinson buffers of pH 2.0 to 12.0 were prepared by using 0.2 M boric acid, 0.05 M citric acid, and 0.1 M trisodium orthophosphate. All the chemicals used are of pure analar grade. Stock solution of Dichlone was prepared by dissolving the required amount in methanol and making up to volume with the supporting electrolyte to obtain the desired concentration. Before running the voltammograms the test solution was purged with purified nitrogen for 10 min. A 0.02% aqueous solution of Triton X-100 was used to eliminate the polarographic maxima.

EXPERIMENTAL PROCEDURE

A standard stock solution of Dichlone ($1 \times 10^{-3} \text{ M}$) was prepared by dissolving the required amount in methanol and making up to volume with the supporting electrolyte to obtain the desired concentration. 1ml of the standard solution is transferred into a polarographic cell and made up with 9 ml of the supporting electrolyte by 10 times dilution sensitivity is decreased and the solution is deoxygenated with oxygen-free nitrogen gas for 10 min. After recording the polarograms, small increments (0.2ml standard solution) are added and the polarograms are recorded after each addition under similar conditions. The optimum conditions for the analytical determination of Dichlone in pH 4.0 were found to be drop time 1.4s, pulse amplitude 50mv and applied potential of -0.40 v. The related standard deviations and correlation co-efficient for 10 replicates are found to be 1.56% and 0.991 for Dichlone.

RESULTS AND DISCUSSION

Characterization of wave/peak

The electrochemical behaviour of Dichlone has been examined over the pH range 2.0 to 12.0. It exhibits a single well defined wave/peak in the entire pH range. The wave/peak is attributed to the reduction of the quinone group to the corresponding hydroquinone in a two electron process. In cyclic voltammetry, an anodic peak (a) is observed in the reverse scan. This anodic peak may be ascribed to the oxidation of the formed hydroquinone to the corresponding quinone. Typical voltammograms are shown in Figures 2 - 5.

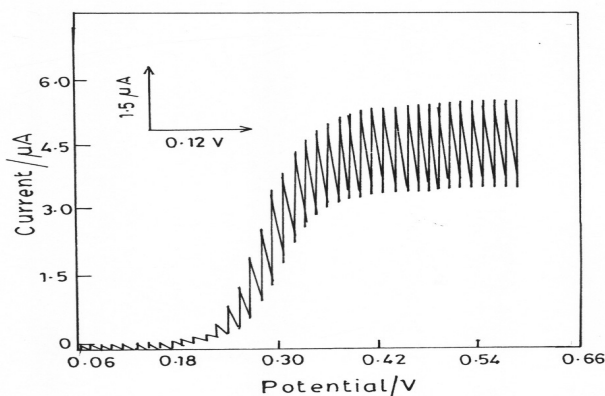
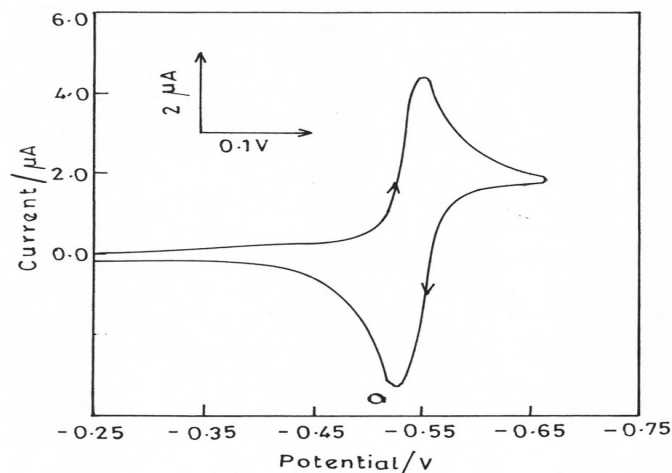
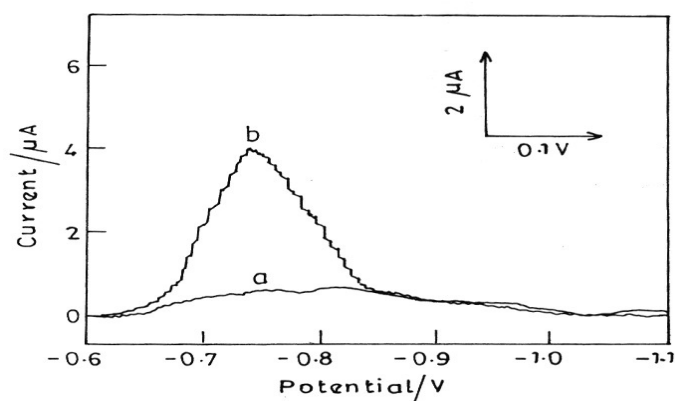


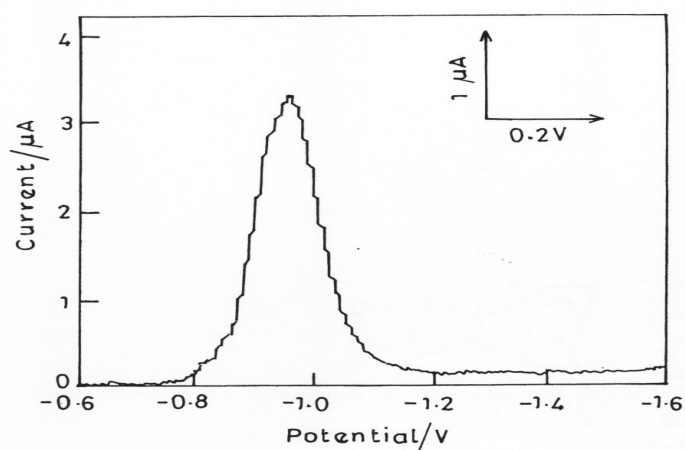
Figure 2: Typical d.c. polarograms of dichlone in pH 2.0 Concentration: 0.5mM Drop time: 3s



**Figure 3: Typical cyclic voltammogram of dichlone in pH 6.0 Concentration:0.5mM
Scan rate:40 mVs⁻¹**



**Figure 4: Typical a.c. polarograms of dichlone in pH 10.0 Concentration: 0.5 mM Drop
time: 3s
a: a.c peak b: base peak**



**Figure 5: Typical differential pulse polarograms of dichlone in pH 4.0 Concentration:
0.5 mM Drop time: 1.4s Pulse amplitude: 50 mV**

Nature of the Electrode Process

The diffusion controlled adsorption free nature of the electrode process is evidenced from the linear plots of i_d vs $h^{1/2}$ (Figure. 6) i_p vs $v^{1/2}$ (Figure. 7) and i_m vs $t^{2/3}$ (Figure. 8) passing through origin in all supporting electrolytes ranging from pH 2.0 to 12.0. A.C. polarographic measurements have also indicated the process to be adsorption free in all the buffer systems as seen from the base current values. The experimental constancy $i_p/v^{1/2}$ with scan rate (V) in cyclic voltammetry indicates that the electrode processes is free any kinetic complications.

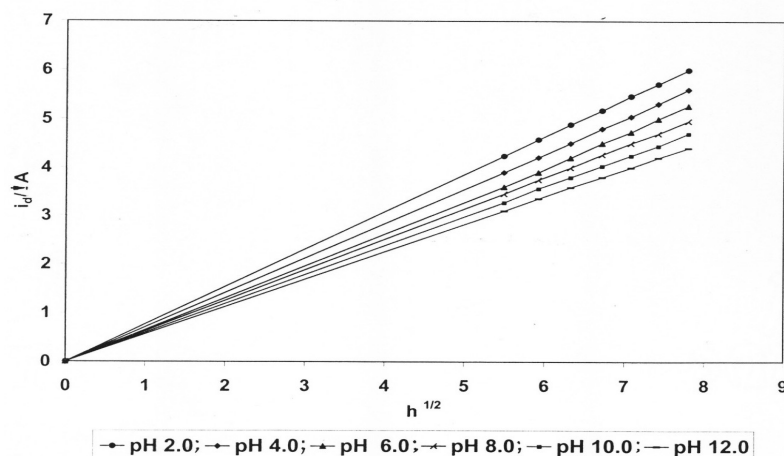


Figure 6: i_d vs $h^{1/2}$ plots of Dichlone Concentration: 0.5mM

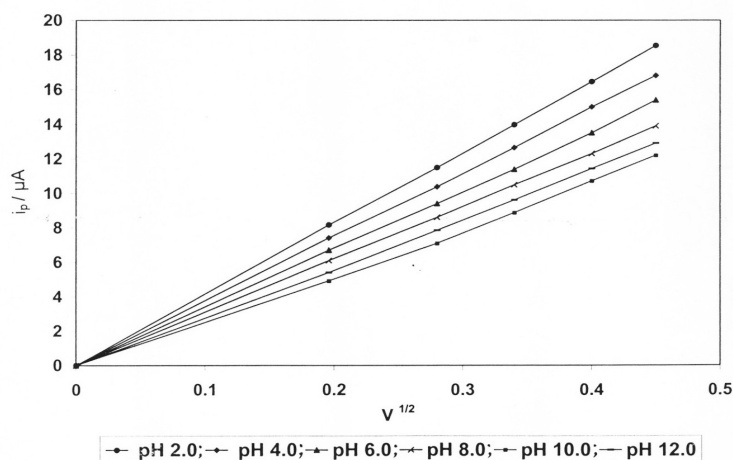


Figure 7: i_p vs $v^{1/2}$ plots of Dichlone Concentration: 0.5mM

The $E_{1/2}$ and E_p values of the reduction wave/peak are found to be independent of the concentration of the electroactive species indicating the electrode processes is to be reversible in Dichlone. The reversibility of the electrode process is also verified by the logarithmic analysis of waves. The slope of the E vs $\log(i/i_d - i)$ plot and the numerical values of $E_{1/4} - E_{3/4}$ are found to be almost equal to $56.4/n$ mv of Dichlone. The linearity in the plots of i_m vs $1 - \sigma / 1 + \sigma$ in differential pulse polarography and the presence of anodic peak in cyclic voltammetric reverse scan also confirm that the reduction processes are reversible.

The half – wave and peak potential are shifted towards more negative potentials with increasing in pH of the buffer solution indicating the participation of proton in the reduction process. The number of protons involved in rate determining step is calculated from $E_{1/2}$ vs pH plot and is found to be one for the reduction process.

Identification of the product

Millicoulometry is employed to find out the number of electrons involved in the electrode process. It is found to be two in acidic (pH 2.0) and basic medium (pH 12.0). Controlled potential electrolysis (CPE) has been carried with mercury pool cathode, saturated calomel electrode as reference electrode and platinum wire electrode as counter electrode. About 50 mg of the electroactive species under investigation is dissolved in a minimum amount of methanol and added to the cell containing supporting electrolyte (pH 4.0). The applied potential is fixed at -0.45 V for Dichlone. The electrolysis is carried out approximately for 4 hours. The product formed after controlled potential electrolysis is identified as the corresponding hydroquinone by IR spectral studies (The characteristic peaks for hydroxyl group O-H stretch broad peak 3342 cm^{-1} , O-H bend: 1368 cm^{-1} and C-O stretch: 1232 cm^{-1}) is shown in figure 9.

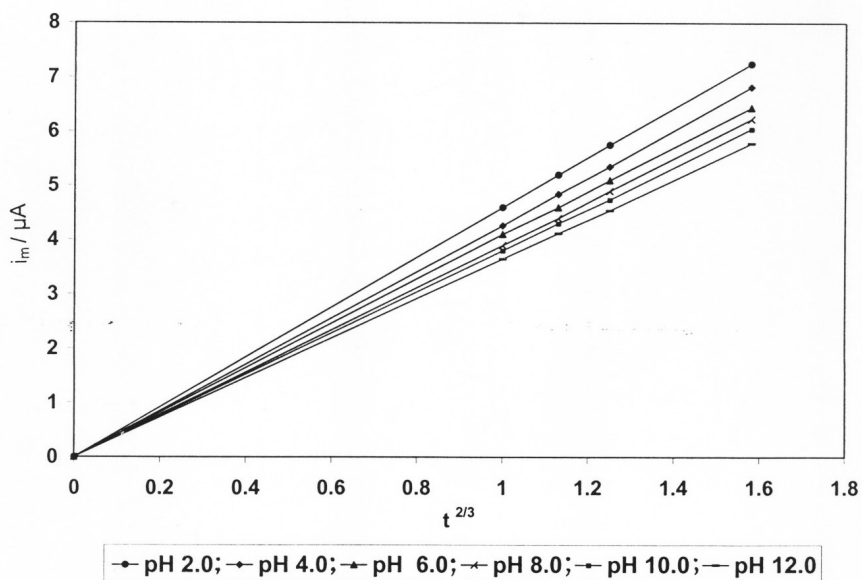


Figure 8: i_m vs $t^{2/3}$ plots of Dichlone Concentration: 0.5mM

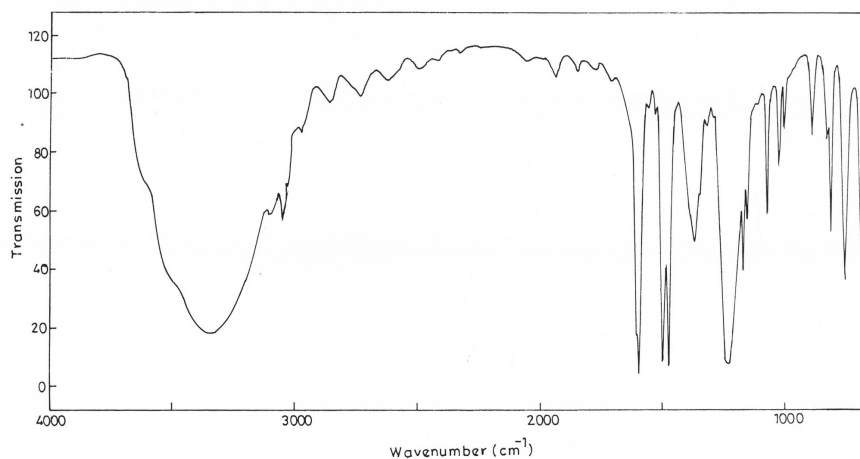


Figure 9: I.R. Spectrum of the reduction product of dichlone

Kinetic data

Diffusion coefficient values calculated at various pH values in various techniques are shown in Table 1 to 4. The adsorption free nature of the electrode process is clearly evidenced from the nearly equal diffusion coefficient values obtained from all the techniques for Dichlone. The diffusion coefficient values were seen to decrease gradually, which account for the decrease in diffusion current with increase in pH due to less availability of protons.

**Table 1: Typical d.c. polarographic data of Dichlone Concentration: 0.5mM,
Drop time: 3s,**

pH of the supporting electrolyte	$-E_{1/2}/V$	$i_d/\mu A$	$D \times 10^6/cm^2 s^{-1}$
2.0	0.29	5.2	4.97
4.0	0.42	4.9	3.92
6.0	0.51	4.5	3.62
8.0	0.64	4.4	3.40
10.0	0.76	4.0	3.26
12.0	0.85	3.9	3.02

**Table 2: Typical cyclic voltammetric data of Dichlone, Concentration: 0.5 mM,
Scan rate: 40 mV s⁻¹**

pH of the supporting electrolyte	$-E_p/V$	$i_p/\mu A$	$D \times 10^6/cm^2 s^{-1}$
2.0	0.31	5.1	4.88
4.0	0.43	4.6	3.98
6.0	0.53	4.4	3.56
8.0	0.67	4.1	3.42
10.0	0.78	3.9	3.36
12.0	0.85	3.7	3.01

**Table 3: Typical a.c. polarographic data of Dichlone Concentration:0.5mM,
Drop time: 3s,**

pH of the supporting electrolyte	$-E_s/V$	$i_s/\mu A$	$D \times 10^6/cm^2 s^{-1}$
2.0	0.26	5.3	4.92
4.0	0.37	4.8	4.01
6.0	0.51	4.4	3.91
8.0	0.63	4.2	3.84
10.0	0.75	3.9	3.15
12.0	0.86	3.6	2.99

Table 4: Typical differential pulse polarographic data of Dichlone Concentration: 0.5mM, Drop time: 1.4s, Pulse amplitude: 50 mV

pH of the supporting electrolyte	$-E_m/V$	$i_m/\mu A$	$D \times 10^6/cm^2 s^{-1}$
2.0	0.27	5.5	4.92
4.0	0.40	5.1	4.14
6.0	0.49	4.7	3.92
8.0	0.60	4.4	3.81
10.0	0.69	4.1	3.21
12.0	0.81	3.8	2.97

Electrode mechanism.

Based on the above results and observation obtained in the present investigation, as well as from the literature [8] the following reduction mechanism may be proposed to the compound in the entire pH range Figure 10.

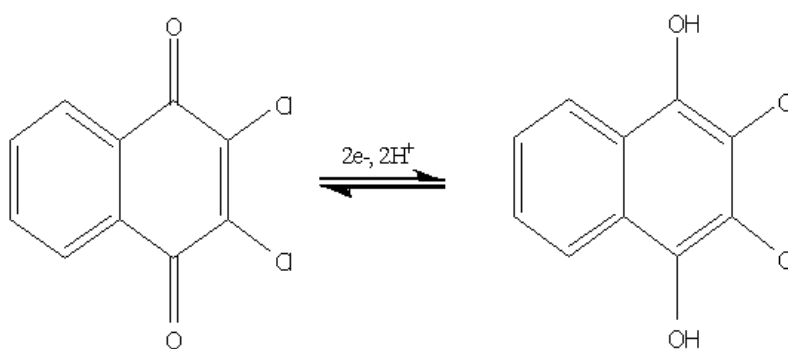


Figure 10: Scheme for Electrode Mechanism of Dichlone

ANALYSIS

In the present investigation differential pulse polarography has been employed to work out analytical procedures for the estimation of Dichlone in grains, soil and water samples using both calibration and standard addition methods. Investigated compound is found to exhibit well resolved peak in pH 4.0 which is chosen for quantitative studies. The peak currents were found to vary linearly with the concentration of the depolarizer over the concentration range 1.0×10^{-5} M to 3.0×10^{-8} M for Dichlone. The detection limit is found to be 2.8×10^{-8} M, which are calculated from the expression $dl = 3Sd/m$

where 'dl' is the lower detection limit

'Sd' is the standard deviation and

'm' is the slope of the calibration plot.

Analysis of Dichlone in grains

Sample is spiked with known amount of standard grain (rice, 50g), which are previously made in the form of loose powder and left for 2-4 hrs. The samples are extracted with dichloromethane twice each time with 30ml. Then the mixture is transferred into Buchner funnel and filtered under suction. The extract is taken into a separating funnel to which 30 ml of water, 10 ml of saturated sodium chloride and 30 ml of dichloromethane are added and thoroughly shaken for 2 min. The combined extracts were filtered over 50 g of anhydrous sodium sulphate and the solvent is evaporated through rotatory evaporator. The residues are dissolved in methanol and transferred into 50 ml volumetric flask. A recovery of Dichlone in grain samples are incorporated in Table 5.

Table 5: Recoveries of Dichlone added to grains and soils, Pulse amplitude: 50mV, Drop time: 1.4 s

Amount added (mg)	Average amount found [†] (mg) ± SD		Average recovery (%)	
	Rice	Soil	Rice	Soil
5.0	4.90±0.040	4.94±0.038	98.00	98.80
10.0	9.89±0.036	9.93±0.030	98.90	99.30
15.0	14.93±0.028	14.94±0.045	99.53	99.60
20.0	19.89±0.023	19.86±0.015	99.45	99.30

*Each value is an average of four determinations

Analysis of Dichlone in soil

Soil samples are dried in a filter paper at laboratory temperature, allowed to pass through a 2.8 m sieve and homogenized in a ball mill. An aliquot (10g) of soil sample is spiked with known amounts of Dichlone solution and left for 2-4 hrs. These are extracted with hexane three times. Each time 50ml of hexane is used. The combined extracts are dried over anhydrous sodium sulphate and the solvent is removed through evaporation. The residue was dissolved in methanol and transferred into 50 ml standard flask. Recoveries of Dichlone in soil samples are presented in Table 5.

Analysis of Dichlone in water sample

A 1000 ml of water samples (Tap and well water) is spiked with the known amounts of the Dichlone left for 1hr. An aliquot of the solution was passed through a Whatmann Nylon membrane filter (0.45 pore size) and the filtrates are passed through a Sep-Pak C18 cartridge previously activated with 10 ml of acetonitrile and 5ml of deionised water. Elutions were carried out with 10 ml of acetonitrile and filtered through anhydrous sodium sulphate. The organic phase is evaporated to dryness in rotatory vacuum evaporator. The residues are dissolved in methanol and added to cell containing buffer solution. The results obtained from the water samples are shown in Table 6.

Table 6: Recoveries of Dichlone added to water samples, Pulse amplitude: 50mV, Drop time: 1.4 s

Sample type	Amount added (M)	Average amount found [†] (M)	Average recovery (%)
Tap water	2×10^{-6}	1.93×10^{-6}	96.50
	4×10^{-6}	3.90×10^{-6}	97.50
Well water	6×10^{-6}	5.91×10^{-6}	98.50
	8×10^{-6}	7.89×10^{-6}	98.62

*Each value is an average of four determinations

CONCLUSION

The results indicate that the above proposed methods are simple, rapid and sensitive with reasonable precision and accuracy which makes it as choice for routine quality control analysis. There is no interference of excipients present in environmental samples through out the experimental process that reflects the accuracy and precision of method.

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